



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) **EP 0 744 444 A3**

(12) **EUROPEAN PATENT APPLICATION**

(88) Date of publication A3:  
08.04.1998 Bulletin 1998/15

(51) Int Cl.<sup>6</sup>: **C08L 83/07, C08K 3/22,  
C08L 83/04**

(43) Date of publication A2:  
27.11.1996 Bulletin 1996/48

(21) Application number: **96303647.0**

(22) Date of filing: **22.05.1996**

(84) Designated Contracting States:  
**DE FR GB IT**

(30) Priority: **24.05.1995 JP 149402/95**

(71) Applicant: **Dow Corning Toray Silicone Co., Ltd.  
Chuo-ku, Tokyo (JP)**

(72) Inventors:  
• **Nakamura, Akito,  
c/o Dow C. Toray Silicone Co. Ltd  
Ichihara-shi, Chiba Pref. (JP)**

• **Tsuji, Yulchi, c/o Dow C. Toray Silicone Co., Ltd.  
Ichihara-shi, Chiba Pref. (JP)**

(74) Representative: **Kyle, Diana  
Elkington and Fife  
Prospect House  
8 Pembroke Road  
Sevenoaks, Kent TN13 1XR (GB)**

(54) **Liquid silicone rubber composition for lubricant seal**

(57) A liquid silicone rubber composition for a lubricant seal having after it is cured high resistance to lubricant, with high stability displayed even in a lubricant that has been subjected to thermal and oxidative degradation, and having its rubber elasticity well maintained. This composition for use a lubricant seal comprises the following ingredients: (A) an organopolysil-

loxane containing 2 or more silicon-bonded alkenyl groups in each molecule; (B) an inorganic filler; (C) an oxide or hydroxide of an alkaline-earth metal with an atomic weight of 40 or greater; (D) an organohydrogen-siloxane containing 3 or more silicon-bonded hydrogen atoms in each molecule; and (E) a platinum-group catalyst.

**EP 0 744 444 A3**

European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 96 30 3647

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	EP 0 572 148 A (GEN ELECTRIC) 1 December 1993 * page 6, line 35 - page 6, line 42 * * examples IV, VIII * * page 13, line 50 - page 13, line 53 * * claim 1 *	1-6	C08L83/07 C08K3/22 C08L83/04
Y	EP 0 415 180 A (GEN ELECTRIC) * page 6, line 19 - page 6, line 25 * * table IV *	1-6	
Y	US 4 681 913 A (EVANS EDWIN R ET AL) 21 July 1987 * column 4, line 19 - column 4, line 45 * * example 2 * * claims 1,5 *	1-6	
Y	US 4 640 956 A (TOUB MELVIN R ET AL) 3 February 1987 * column 2, line 44 - column 3, line 19 * * claims 1,3 *	1-6	
A	US 3 839 266 A (BARGAIN M) 1 October 1974 * claims 1,15 *	1-6	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C08K C08L
A	EP 0 234 271 A (DOW CORNING) 2 September 1987 * page 6, line 15 - page 6, line 56 * * example 1 * * claim 3 *	1-6	
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 30 January 1998	Examiner Heidenhain, R
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document		T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document	

EPO FORM 1503 03.92 (P/MC201)



(19)

Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

**EP 0 744 444 A2**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
27.11.1996 Bulletin 1996/48

(51) Int Cl.<sup>6</sup>: C08L 83/07, C08K 3/22

(21) Application number: 96303647.0

(22) Date of filing: 22.05.1996

(84) Designated Contracting States:  
DE FR GB IT

(30) Priority: 24.05.1995 JP 149402/95

(71) Applicant: Dow Corning Toray Silicone Co., Ltd.  
Chuo-ku, Tokyo (JP)

(72) Inventors:  
• Nakamura, Akito,  
c/o Dow C. Toray Silicone Co. Ltd  
Ichihara-shi, Chiba Pref. (JP)

• Tsuji, Yuichi, c/o Dow C. Toray Silicone Co., Ltd.  
Ichihara-shi, Chiba Pref. (JP)

(74) Representative: Kyle, Diana  
Elkington and Fife  
Prospect House  
8 Pembroke Road  
Sevenoaks, Kent TN13 1XR (GB)

(54) **Liquid silicone rubber composition for lubricant seal**

(57) A liquid silicone rubber composition for a lubricant seal having after it is cured high resistance to lubricant, with high stability displayed even in a lubricant that has been subjected to thermal and oxidative degradation, and having its rubber elasticity well maintained. This composition for use a lubricant seal comprises the following ingredients: (A) an organopolysil-

oxane containing 2 or more silicon-bonded alkenyl groups in each molecule; (B) an inorganic filler; (C) an oxide or hydroxide of an alkaline-earth metal with an atomic weight of 40 or greater; (D) an organohydrogen-siloxane containing 3 or more silicon-bonded hydrogen atoms in each molecule; and (E) a platinum-group catalyst.

EP 0 744 444 A2

## Description

This invention pertains to a liquid silicone rubber composition useful as a lubricant seal. This novel composition is characterized by the fact that it has high stability against a lubricant that has been subjected to thermal and oxidative degradation.

Silicone rubber has high heat resistance, high cold resistance, and low compression set. Consequently, it is widely used to form seals in automobiles, ships, and industrial machines. For various seals, including rocker covers, oil pans, oil filters, shafts, and the like which are in direct contact with a lubricant, wherein the resistance to lubricant that has been degraded by heat and oxidation is high. Thus, these seals are required to display high stability to the acid components generated by degradation of the lubricant, to residues of various additives, and to oxygen dissolved in the lubricant. Conventional silicone rubber does not have as good of stability in such an environment as is often desired.

In consideration of this problem, various methods to increase the oil resistance of the silicone rubber composition have been proposed by adding various types of basic substances into it. For example, JP-A 57-76055 discloses a method in which magnesium oxide powder is added into silicone rubber composition that is then cured by a condensation reaction to obtain a silicone rubber which is cured at room temperature and which has a high oil resistance. Also, JP-A 3-149260 discloses a method in which magnesium oxide powder is added into a silicone rubber composition that is cured in the presence of a platinum catalyst to obtain a silicone rubber with a high oil resistance.

However, for the former method, a long curing time is needed at room temperature to obtain the desired silicone rubber. The workability is thus poor, and the silicone rubber also has low mechanical strength.

For the latter method, when a large amount of magnesium oxide powder is added (a highly basic substance) the platinum catalyst may be poisoned. In addition, in the presence of organohydrogenpolysiloxane, that composition may begin to cure during storage. Even when the material is stored as a 2-part liquid system, it is still impossible to guarantee a high storage stability and a long pot life; and it is impossible to increase the amount of the magnesium oxide powder added. Consequently, high oil resistance is not realized and the durability of the cured silicone rubber is poor when used under severe operating conditions of thermally and oxidatively degraded lubricants.

The purpose of this invention is to provide a liquid silicone rubber composition for a lubricant seal characterized by good storage stability and long pot life before curing, and when cured having good stability and ability to maintain excellent rubber elasticity, even in the presence of lubricant that has been subjected to thermal and oxidative degradation.

The liquid silicone rubber composition for a lubricant seal of this invention has the following ingredients: (A) an organopolysiloxane containing 2 or more silicon-bonded alkenyl groups in each molecule; (B) an inorganic filler; (C) an oxide or hydroxide of an alkaline-earth metal with an atomic weight of 40 or greater; (D) an organohydrogensiloxane containing 3 or more silicon-bonded hydrogen atoms in each molecule; and (E) a platinum-group catalyst.

The present invention provides a liquid silicone rubber composition for a lubricant seal comprising the following ingredients:

- (A) 100 parts by weight of organopolysiloxane containing 2 or more silicon-bonded alkenyl groups in each molecule;
- (B) 5 to 150 parts by weight of inorganic filler;
- (C) 7 to 50 parts by weight of an oxide or hydroxide of an alkaline-earth metal with an atomic weight of 40 or greater;
- (D) an organohydrogensiloxane containing 3 or more silicon-bonded hydrogen atoms in each molecule in an amount providing a molar ratio of the silicon-bonded hydrogen atoms in this ingredient to the silicon-bonded alkenyl groups in ingredient (A) in the range of 0.4:1 to 5:1; and
- (E) a platinum-group catalyst in an amount providing 0.1 to 500 parts by weight of platinum-group metal per 1 million parts by weight of ingredient (A).

Ingredient (A), the organopolysiloxane, is the basic ingredient of the present composition. In order to ensure that our silicone rubber composition can display rubber elasticity after curing, it is necessary that 2 or more alkenyl groups are present in each molecule of the organopolysiloxane. Examples of alkenyl groups are vinyl, allyl, and propenyl. Examples of organic groups, other than these alkenyl groups, include alkyl groups like methyl, ethyl, and propyl; aryl groups such as phenyl or tolyl and halogenated alkyl groups like 3,3,3-trifluoropropyl, 3-chloropropyl; and other optionally substituted monovalent hydrocarbon groups.

The molecular configuration of this ingredient may be straight-chained, branch-containing straight-chain, or cyclic. The straight-chained form is preferred. There is no special limitation on the viscosity of this ingredient. To ensure that the cured product is a rubber-like elastic body, the viscosity of this ingredient at 25°C is preferably 100 mPa.s (cP) or higher. Examples of this ingredient include dimethylpolysiloxane with both ends blocked by dimethylvinylsiloxy groups, dimethylsiloxane/methylvinylsiloxane copolymer with both ends blocked by dimethylvinylsiloxy groups, dimethylsiloxane/methylvinylsiloxane copolymer with both ends blocked by trimethylsiloxy groups, and dimethylsiloxane/methylphenylsiloxane copolymer with both ends blocked by dimethylvinylsiloxy groups. According to this invention, it is

possible to use two or more types of the aforementioned organopolysiloxanes in combination.

Ingredient (B), the inorganic filler, is used to reinforce our silicone rubber composition, adjust the viscosity, increase the heat resistance, increase the flame retardancy, and so forth. There is no special limitation on the type of inorganic filler, and any conventional one can be used. Examples of such fillers are fumed silica, precipitated silica, sintered silica, fumed titanium oxide, and other reinforcing fillers; crushed fused silica, diatomaceous earth, asbestos, iron oxide, aluminum oxide, aluminosilicic acid, calcium carbonate, and other nonreinforcing fillers; as well as fillers prepared by treating the aforementioned fillers with an organosilane, organopolysiloxane, or other organic silicon compound. The amount of this ingredient added depends on the type of the inorganic filler used. Usually, the amount of this ingredient is in the range of 5 to 150 parts by weight per 100 parts by weight of ingredient (A).

Ingredient (C), the oxide or hydroxide of an alkaline-earth metal with an atomic weight of 40 or greater, is the characteristic ingredient of this invention. This ingredient is added to ensure that the cured product of our composition has a high stability in degraded oil. That is, a high stability against the chemical species caused by the acid components generated by the degradation of the oil component, residues of the various types of additives present in the oil, and dissolved oxygen present in the oil. Examples of the oxides and hydroxides of alkaline-earth metals include the oxides and hydroxides of calcium, strontium, and barium. They may be used either alone or as a mixture of two or more. Also, they may be used in the form of fine powders to ensure their effective dispersion in our silicone composition. Among them, calcium hydroxide and calcium oxide are preferred. The amount of this ingredient with respect to 100 parts by weight of ingredient (A) is in the range of 7 to 50 parts by weight, or preferably in the range of 10 to 40 parts by weight. If the amount is smaller than 7 parts by weight, the resultant composition fails to display a high enough resistance to the degraded oil. On the other hand, if the amount is over 50 parts by weight, the viscosity of the final composition becomes too high thereby making handling difficult and decreasing the strength of the cured rubber product.

Ingredient (D), the organohydrogensiloxane containing 3 or more silicon-bonded hydrogen atoms in each molecule, is a crosslinking agent. Examples of organohydrogensiloxanes that are used include methylhydrogenpolysiloxane with both ends blocked by trimethylsiloxy groups, dimethylsiloxane/methylhydrogensiloxane copolymer with both ends blocked by trimethylsiloxy groups, methylphenylsiloxane/methylhydrogensiloxane copolymer with both ends blocked by dimethylphenylsiloxy groups, cyclic methylhydrogenpolysiloxane, and a copolymer made of dimethylhydrogen siloxy units and  $\text{SiO}_{4/2}$  units. The amount of organohydrogensiloxane added is appropriate to ensure that the molar ratio of the silicon-bonded hydrogen atoms in this ingredient to the silicon-bonded alkenyl groups in ingredient (A) is in the range of 0.4:1 to 5:1. Otherwise, it is impossible to obtain good curing properties.

Ingredient (E), the platinum-group catalyst, is a catalyst for curing our claimed the composition. Examples of useful catalysis include fine platinum powder, platinum black, chloroplatinic acid, platinum tetrachloride, olefin complexes of chloroplatinic acid, alcohol solutions of chloroplatinic acid, complexes of chloroplatinic acid and alkenylsiloxanes, or like compounds of rhodium and palladium. The amount of the platinum-group catalyst added is usually that providing 0.1 to 800 parts by weight of platinum-type metal atoms per 1 million parts by weight of ingredient (A). If the amount is smaller than 0.1 part, the curing reaction may not proceed sufficiently; if the amount is over 500 parts, the cost effectiveness is very poor.

Ingredient (E) is preferably in the form of a spherical-shaped fine-grain catalyst made of a thermoplastic resin containing 0.01 wt% or more of platinum metal atoms, as there is no catalyst poisoning effect caused by ingredient (C). Also, to ensure that the platinum-type catalyst ingredient is dispersed fast in our composition at the conventional molding temperature, the softening point of the thermoplastic resin should be in the range of 50 to 150°C. Also, the average grain size of the spherical-shaped fine-grain catalyst is in the range of 0.01 to 10  $\mu\text{m}$ .

The composition of this invention is easily manufactured by uniformly blending ingredients (A) through (E), as well as various additives as demanded, such as heat resistance agents, flame-retarding agents, and pigments. This blending can be performed by means of a kneader mixer, a pressurized kneader mixer, Ross™ mixer, and other blenders. The composition may also be prepared as two or more liquids, which are blended immediately before use, to facilitate manufacturing and to improve the workability.

In the following, this invention will be explained in more detail with reference to specific examples. In the examples, parts refer to parts by weight and the viscosity refers to the value at 25°C.

#### Example 1.

100 parts of a dimethylpolysiloxane (with vinyl group content of 0.23 wt%) that has both ends of the molecular chain blocked by dimethylphenylsiloxy groups and has a viscosity of 2,000 mPa.s (cP), 13 parts of crushed fused silica with an average grain size of 5  $\mu\text{m}$ , and 30 parts of fumed silica that has been surface-treated with dimethyldichlorosilane and has a specific surface area of 200  $\text{m}^2/\text{g}$  were blended until the mixture became homogeneous. After heat treatment under vacuum, 12 parts of finely powdered calcium hydroxide were added, followed by blending to homogeneity to form a flowable liquid silicone rubber base.

Then, 100 parts of the liquid silicone rubber base were blended uniformly with the following ingredients to form a

liquid silicone rubber composition: 1.7 parts of dimethylsiloxane/methylhydrogensiloxane copolymer (with 0.8 wt% silicon-bonded hydrogen atoms), 0.3 part of spherical-shaped fine-grain catalyst of thermoplastic resin containing a complex of chloroplatinic acid and tetramethyldivynilsiloxane in an amount corresponding to 0.4 wt% of platinum metal atoms (product of Toray Dow Corning Silicone Co., Ltd., with an average grain size of 1.1  $\mu\text{m}$  and a softening point of the thermoplastic resin of 85°C), and 0.01 part of 3,5-dimethyl-1-hexyn-3-ol as a curing inhibitor.

The silicone rubber composition was press molded at 150°C for 5 minutes to form rubber sheet specimens for measurement of properties as defined in JIS K 6301. The initial properties were then measured (time=0). Then, the resistance of the specimens against degraded oil (a lubricant that had been degraded by heat and oxidation) was measured. The resistance to degraded oil was measured by the following method: automotive engine oil (a product of Toyota Motor Corp.; commercial name: Castle Motor Oil Green SG 10W-30) was used to fill 75% of the interior volume of a pressure-proof container. After the specimen was placed in the oil, oxygen gas was filled at a pressure of 10 kg/cm<sup>2</sup> to occupy the remaining space of the container. The container was sealed and placed in an oven at 150°C for heating. The container was taken out from the oven every 24 hours and refilled with oxygen under a pressure of 10 kg/cm<sup>2</sup> at room temperature and replaced in the oven. After this operation had been carried out repeatedly for prescribed times (time=72, 240, or 360 hours), the specimens were taken out of the degraded oil and the physical properties were measured.

For comparison, a silicone rubber composition was prepared in the same way as above, except that crushed fused silica with an average grain size of 5  $\mu\text{m}$  was used. Then, the physical properties were measured as described above. The results are listed in Table I.

Table I. Results of Test of Resistance to Degraded Oil

Time (h)	Property	Elastomer	
		Test	Comparison
0	Hardness (JIS A <sub>2</sub> )	52	52
	Tensile (Kgf/cm <sup>2</sup> )	44	54
	Elongation (%)	260	320
72	Hardness (JIS A <sub>2</sub> )	40	39
	Tensile (Kgf/cm <sup>2</sup> )	37	41
	Elongation (%)	200	210
240	Hardness (JIS A <sub>2</sub> )	37	10
	Tensile (Kgf/cm <sup>2</sup> )	35	13
	Elongation (%)	210	350
60	Hardness (JIS A <sub>2</sub> )	36	2
	Tensile (Kgf/cm <sup>2</sup> )	30	1
	Elongation (%)	260	100

#### Example 2.

A silicone rubber composition was prepared in the same way as described in Example 1, except that 12 parts of finely powdered calcium oxide were used. The physical properties of the cured specimens were also measured in the same way as in Example 1. For comparison, a silicone rubber composition was prepared in the same way as above, except that the amount of the finely powdered calcium oxide was reduced to 5 parts. The physical properties of the cured specimens were also measured in the same way as described above. The results for these tests are listed in Table II.

Table II.

Results of Test of Resistance to Degraded Oil			
Time (h)	Property	Elastomer	
		Test	Comparison
0	Hardness (JIS A)	48	50
	Tensile (Kgf/cm <sup>2</sup> )	49	51

Table II. (continued)

Results of Test of Resistance to Degraded Oil			
Time (h)	Property	Elastomer	
		Test	Comparison
	Elongation (%)	350	310
72	Hardness (JIS A)	40	39
	Tensile (Kgf/cm <sup>2</sup> )	44	42
	Elongation (%)	270	200
240	Hardness (JIS A)	31	19
	Tensile (Kgf/cm <sup>2</sup> )	38	27
	Elongation (%)	270	290
360	Hardness (JIS A)	28	7
	Tensile (Kgf/cm <sup>2</sup> )	22	9
	Elongation (%)	300	370

## Example 3.

85 parts of dimethylpolysiloxane (with a vinyl group content of 0.23 wt%) that had both ends of the molecular chain blocked by dimethylvinylsiloxy groups and a viscosity of 2,000 mPa.s (cP), 15 parts dimethylsiloxane/methylvinylsiloxane copolymer (with vinyl group content of 0.52 wt%) with both ends of the molecular chain blocked by trimethylsiloxy groups and a viscosity of 40,000 mPa.s (cP), 30 parts of crushed fused silica with average grain size of 5  $\mu$ m, 30 parts of fumed silica with a specific surface area of 200 m<sup>2</sup>/g, 5 parts of hexamethyldisilazane, and 2 parts of water were uniformly blended and heat treated under vacuum. Then, 20 parts of finely powdered calcium hydroxide were added, and the mixture was blended until it became homogeneous, forming a flowable liquid silicone rubber base.

Next, 100 parts of the above silicone rubber base were blended uniformly with the following ingredients to form a liquid silicone rubber composition: 1.7 parts of dimethylsiloxane/methylhydrogensiloxane copolymer (with 0.8 wt% silicon-bonded hydrogen atoms), 0.3 part of spherical-shaped fine-grain catalyst of thermoplastic resin containing a complex of chloroplatinic acid and tetramethyldivinylsiloxane in an amount corresponding to 0.4 wt% of the platinum metal atoms (product of Toray Dow Corning Silicone Co., Ltd., with an average grain size of 1.1  $\mu$ m and a softening point of the thermoplastic resin of 85°C), and 0.01 part of 3,5-dimethyl-1-hexyn-3-ol as cure inhibitor. The physical properties of cured specimens were also measured as described in Example 1.

For comparison, a silicone rubber composition was prepared in the same way as described above, except that crushed fused silica with an average grain size of 5  $\mu$ m was used. Then, the physical properties were measured as described above. The results are listed in Table III.

Table III.

Results of Test of Resistance to Degraded Oil			
Time (h)	Property	Elastomer	
		Test	Comparison
0	Hardness (JIS A)	65	65
	Tensile (Kgf/cm <sup>2</sup> )	63	59
	Elongation (%)	200	140
72	Hardness (JIS A)	52	50
	Tensile (Kgf/cm <sup>2</sup> )	55	55
	Elongation (%)	150	140
240	Hardness (JIS A)	41	22
	Tensile (Kgf/cm <sup>2</sup> )	39	16
	Elongation (%)	170	200
360	Hardness (JIS A)	36	13
	Tensile (Kgf/cm <sup>2</sup> )	24	4

Table III. (continued)

Results of Test of Resistance to Degraded Oil			
Time (h)	Property	Elastomer	
		Test	Comparison
	Elongation (%)	180	160

# Claims

1. A liquid silicone rubber composition for a lubricant seal comprising the following ingredients:

(A) 100 parts by weight of organopolysiloxane containing 2 or more silicon-bonded alkenyl groups in each molecule;

(B) 5 to 150 parts by weight of inorganic filler;

(C) 7 to 50 parts by weight of an oxide or hydroxide of an alkaline-earth metal with an atomic weight of 40 or greater;

(D) an organohydrogensiloxane containing 3 or more silicon-bonded hydrogen atoms in each molecule, in an amount providing a molar ratio of the silicon-bonded hydrogen atoms in this ingredient to the silicon-bonded alkenyl groups in ingredient (A) of 0.4:1 to 5:1; and

(E) a platinum-group catalyst in an amount providing 0.1 to 500 parts by weight of platinum-group metal per 1 million parts by weight of ingredient (A).

2. The liquid silicone rubber composition described in Claim 1, where ingredient (E) is a spherical-shaped fine-grain catalyst made of a thermoplastic resin containing 0.01 wt% platinum metal atoms, the softening point of the thermoplastic resin is in the range of 50-150°C, and the average grain size of the spherical-shaped fine-grain catalyst is in the range of 0.01 to 10 µm.

3. The liquid silicone rubber composition described in Claim 1, where ingredient (A) is a straight-chained polymer having a viscosity at 25°C of 100 mPa.s (cP) or higher.

4. The liquid silicone rubber composition described in Claim 1, where ingredient (C) is selected from a group consisting of oxides and hydroxides of calcium, strontium, and barium.

5. The liquid silicone rubber composition described in Claim 1, where ingredient (C) is calcium oxide or calcium hydroxide.

6. The liquid silicone rubber composition described in Claim 4, where the amount of ingredient (C) is in the range of 10 to 40 parts by weight per 100 parts by weight of ingredient (A) and ingredient (C) is selected from calcium hydroxide or calcium oxide.